

WHAT IS CLAIMED IS:

*Syk*  
1. A semiconductor element comprising a semiconductor junction composed of silicon-based films, wherein at least one of the silicon-based films contains a microcrystal, and an orientation property of the microcrystal in the silicon-based film containing the microcrystal changes in a film thickness direction of the silicon-based film containing the microcrystal.

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2. The semiconductor element according to claim 1, wherein the semiconductor element is a photovoltaic element including at least one pin type semiconductor junction having a semiconductor layer exhibiting a first conductivity type, i-type semiconductor layers, and a semiconductor layer exhibiting a second conductivity type, the layers being mainly composed of silicon atoms and sequentially stacked on a substrate, wherein at least one of the i-type semiconductor layers includes a silicon-based film containing a microcrystal, and wherein the orientation property of the microcrystal in the silicon-based film is changed in the film thickness direction of the silicon-based film.

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3. The semiconductor element according to claim 2, wherein an amorphous silicon layer is arranged

between the silicon-based film containing the microcrystal and the semiconductor layer exhibiting the first or second conductivity type which is arranged on a light incidence side relative to the silicon-based film.

4. The semiconductor element according to claim 3, wherein the amorphous silicon layer has a film thickness of 30 nm or less.

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5. The semiconductor element according to claim 1, wherein the orientation property of the microcrystal changes so that the ratio of the diffraction intensity of a (220) face of the microcrystal, which is measured with X rays or electron rays, to the total diffraction intensity changes in the film thickness direction of the silicon-based film.

20 6. The semiconductor element according to claim 5, wherein the orientation property of the microcrystal changes so that the ratio of the diffraction intensity of the (220) face of the microcrystal in the silicon-based film containing the microcrystal, which is measured with X rays or electron rays, to the total diffraction intensity is relatively low in an initial stage of film formation.

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7. The semiconductor element according to claim 1, wherein the orientation property of the microcrystal changes continuously.

5           8. The semiconductor element according to claim 1, wherein the silicon-based film containing the microcrystal includes a region in which the diffraction intensity of the (220) face of the microcrystal, which is measured with X rays or  
10 electron rays, occupies 80% or more of the total diffraction intensity.

          9. The semiconductor element according to claim 1, wherein in the silicon-based film containing the  
15 microcrystal, the microcrystal which is preferentially oriented along a (220) face is shaped in a column extending in a vertical direction relative to the substrate.

20        10. The semiconductor element according to claim 1, wherein a microcrystal located in an interface region of the silicon-based film containing the microcrystal is preferentially oriented along the (100) face.

25           11. The semiconductor element according to claim 10, wherein the microcrystal located in the

interface region is shaped in substantially a sphere.

12. The semiconductor element according to claim 10 or 11, wherein a film thickness of the interface region is set to 1.0 nm or more and 20 nm or less.

13. The semiconductor element according to claim 1, wherein the silicon-based film containing the microcrystal contains at least one kind of oxygen atoms, carbon atoms and nitrogen atoms, and the total amount of the atoms is  $1.5 \times 10^{18}$  atoms/cm<sup>3</sup> or more and  $5.0 \times 10^{19}$  atoms/cm<sup>3</sup> or less.

14. The semiconductor element according to claim 1, wherein the silicon-based film containing the microcrystal contains  $1.0 \times 10^{19}$  atoms/cm<sup>3</sup> or more and  $2.5 \times 10^{20}$  atoms/cm<sup>3</sup> or less of fluorine atoms.

15. The semiconductor element according to claim 1, wherein the silicon-based film containing the microcrystal is formed by introducing a source gas containing at least one of a hydrogenated silicon gas and a fluorinated silicon gas, and hydrogen into a vacuum vessel, introducing high frequency into a high frequency introducing section in the vacuum vessel, and forming a silicon-based film on a

substrate introduced into the vacuum vessel by a high frequency plasma CVD process.

16. The semiconductor element according to  
5 claim 15, wherein during the process of forming the silicon-based film containing the microcrystal, the flow rate ratio of the source gas is varied.

17. The semiconductor element according to  
10 claim 15, wherein during the process of forming the silicon-based film containing the microcrystal, the source gas is introduced into the vacuum vessel using a plurality of gas introducing sections, and the source gas flowing through at least one of the  
15 plurality of gas introducing sections has a flow rate ratio different from that in the other gas introducing sections.

18. The semiconductor element according to  
20 claim 15, wherein the high frequency is set to 10 MHz or more and 10 GHz or less.

19. The semiconductor element according to  
claim 18, wherein the high frequency is set to 20 MHz  
25 or more and 300 MHz or less.

20. The semiconductor element according to

claim 15, wherein a distance between the high frequency introducing section and the substrate is set to 3 mm or more and 30 mm or less.

5           21. The semiconductor element according to claim 15, wherein a pressure under which the silicon-based film containing the microcrystal is formed is set to 100 Pa (0.75 Torr) or more and 5,000 Pa (37.5 Torr) or less.

10           22. The semiconductor element according to claim 15, wherein a residence time of the source gas during the formation of the silicon-based film containing the microcrystal is set to 0.01 second or  
15 more and 10 seconds or less.

          23. The semiconductor element according to claim 22, wherein the residence time of the source gas during the formation of the silicon-based film  
20 containing the microcrystal is set to 0.1 second or more and 3 seconds or less.

          24. A semiconductor element comprising a semiconductor junction composed of silicon-based  
25 films, at least one of the silicon-based films containing a microcrystal, wherein the silicon-based film containing the microcrystal is formed by

introducing a source gas containing at least one of a hydrogenated silicon gas and a fluorinated silicon gas, and hydrogen into a vacuum vessel, introducing high frequency into a high frequency introducing section in the vacuum vessel, and forming a silicon-based film on a substrate introduced into the vacuum vessel by using a high frequency plasma process, wherein heating means for the substrate is arranged opposite a surface of the substrate on which the silicon-based film containing the microcrystal is formed, and wherein an output of the heating means decreases as the silicon-based film containing the microcrystal is formed.

25. A method of forming a silicon-based film containing a microcrystal, comprising: forming the film so that the orientation property of the microcrystal changes in a film thickness direction of the silicon-based film containing the microcrystal.

26. The silicon-based film forming method according to claim 25, wherein the orientation property of the microcrystal changes so that the ratio of the diffraction intensity of a (220) face of the microcrystal, which is measured with X rays or electron rays to the total diffraction intensity changes in the film thickness direction of the

silicon-based film.

27. The silicon-based film forming method according to claim 26, wherein the orientation  
5 property of the microcrystal changes so that the ratio of the diffraction intensity of the (220) face of the microcrystal in the silicon-based film containing the microcrystal, which is measured with X rays or electron rays, to the total diffraction  
10 intensity is relatively low in an initial stage of film formation.

28. The silicon-based film forming method according to claim 25, wherein the orientation  
15 property of the microcrystal changes continuously.

29. The silicon-based film forming method according to claim 25, wherein the silicon-based film containing the microcrystal includes a region in  
20 which the diffraction intensity of the (220) face of the microcrystal, which is measured with X rays or electron rays, occupies 80% or more of the total diffraction intensity.

25 30. The silicon-based film forming method according to claim 25, wherein in the silicon-based film containing the microcrystal, the microcrystal



which is preferentially oriented along a (110) face is shaped in a column extending in a vertical direction relative to the substrate.

5           31. The silicon-based film forming method according to claim 25, wherein the microcrystal located in an interface region of the silicon-based film containing the microcrystal is preferentially oriented along the (100) face.

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32. The silicon-based film forming method according to claim 25, wherein the microcrystal located in the interface region is shaped in substantially a sphere.

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33. The silicon-based film forming method according to claim 31 or 32, wherein a film thickness of the interface region is set to 1.0 nm or more and 20 nm or less.

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34. The silicon-based film forming method according to claim 25, wherein the silicon-based film containing the microcrystal contains at least one kind of oxygen atoms, carbon atoms and nitrogen atoms, and the total amount of the atoms is  $1.5 \times 10^{18}$  atoms/cm<sup>3</sup> or more and  $5.0 \times 10^{19}$  atoms/cm<sup>3</sup> or less.

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35. The silicon-based film forming method according to claim 25, wherein the silicon-based film containing the microcrystal contains  $1.0 \times 10^{19}$  atoms/cm<sup>3</sup> or more and  $2.5 \times 10^{20}$  atoms/cm<sup>3</sup> or less of fluorine atoms.

36. The silicon-based film forming method according to claim 25, wherein the silicon-based film containing the microcrystal is formed by introducing source gas containing at least one of a hydrogenated silicon gas and a fluorinated silicon gas, and hydrogen into a vacuum vessel, introducing high frequency into a high frequency introducing section in the vacuum vessel, and forming a silicon-based film on a substrate introduced into the vacuum vessel by a high frequency plasma CVD process.

37. The silicon-based film forming method according to claim 36, wherein during the process of forming the silicon-based film containing the microcrystal, the flow rate ratio of the source gas is varied.

38. The silicon-based film forming method according to claim 36, wherein the source gas is introduced into the vacuum vessel using a plurality of gas introducing sections, and the source gas

flowing through at least one of the plurality of gas introducing sections has a flow rate ratio different from that in the other gas introducing sections.

5           39. The silicon-based film forming method according to claim 36, wherein the high frequency is set to 10 MHz or more and 10 GHz or less.

10           40. The silicon-based film forming method according to claim 39, wherein the high frequency is set to 20 MHz or more and 300 MHz or less.

15           41. The silicon-based film forming method according to claim 36, wherein the distance between the high frequency introducing section and the substrate is set to 3 mm or more and 30 mm or less.

20           42. The silicon-based film forming method according to claim 36, wherein a pressure under which the silicon-based film containing the microcrystal is formed is set to 100 Pa (0.75 Torr) or more and 5,000 Pa (37.5 Torr) or less.

25           43. The silicon-based film forming method according to claim 36, wherein a residence time of the source gas during the formation of the silicon-based film containing the microcrystal is set to 0.01

second or more and 10 seconds or less.

44. The silicon-based film forming method according to claim 43, wherein the residence time of  
5 the source gas during the formation of the silicon-based film containing the microcrystal is set to 0.1 second or more and 3 seconds or less.

45. A method of forming a silicon-based film  
10 containing a microcrystal, comprising: introducing source gas containing at least one of a hydrogenated silicon gas and a fluorinated silicon gas, and hydrogen into a vacuum vessel, introducing high frequency into a high frequency introducing section  
15 in the vacuum vessel, and using a high frequency plasma process to form a silicon-based film on a substrate introduced into the vacuum vessel, wherein heating means for the substrate is arranged opposite a surface of the substrate on which the silicon-based  
20 film containing the microcrystal is formed, and an output of the heating means decreases as the silicon-based film containing the microcrystal is formed.

46. A semiconductor element comprising a  
25 semiconductor junction composed of silicon-based films, wherein at least one of the silicon-based films contains a microcrystal, and a microcrystal

located in at least one interface region of the silicon-based films containing the microcrystal has no orientation property.

5           47. The semiconductor element according to claim 46, wherein the semiconductor element includes at least one pin type semiconductor junction having a semiconductor layer exhibiting a first conductivity type, i-type semiconductor layers, and a  
10 semiconductor layer exhibiting a second conductivity type, the layers being mainly composed of silicon atoms and sequentially stacked on a substrate.

15           48. The semiconductor element according to claim 47, wherein an amorphous silicon layer is arranged between the silicon-based film containing the microcrystal and the semiconductor layer exhibiting the first or second conductivity type which is arranged on a light incidence side relative  
20 to the silicon-based film.

25           49. The semiconductor element according to claim 48, wherein the amorphous silicon layer has a film thickness of 30 nm or less.

50. The semiconductor element according to claim 46, wherein in the silicon-based film

containing the microcrystal, the ratio of the diffraction intensity of a (220) face of the microcrystal except for a non-orientation property region, which is measured with X rays or electron rays, to the total diffraction intensity changes in a film thickness direction of the silicon-based film.

51. The semiconductor element according to claim 1, wherein the orientation property of the microcrystal located in the interface region is such that when measured with X rays or electron rays, three diffraction faces (111), (220), and (311) arranged in this order from the small angle side have such diffraction intensities that when the (111) face has a diffraction intensity of 1, the (220) face has a diffraction intensity of 0.50 or more and 0.60 or less, whereas the (311) face has a diffraction intensity of 0.25 or more and 0.35 or less.

52. The semiconductor element according to claim 50, wherein the ratio of the diffraction intensity of the (220) face of the microcrystal in the silicon-based film containing the microcrystal, which is measured with X rays or electron rays, to the total diffraction intensity is relatively low in an initial stage of film formation.

53. The semiconductor element according to claim 50, wherein the orientation property of the crystal changes continuously.

54. The semiconductor element according to claim 46, wherein the silicon-based film microcrystal includes a region in which the diffraction intensity of the (220) face of the microcrystal, which is measured with X ray diffraction rays, occupies 80% or more of the total diffraction intensity.

55. The semiconductor element according to claim 46, wherein in the silicon-based film defining the microcrystal, a microcrystal is substantially oriented along the (220) face direction in a column extending in a vertical direction relative to the substrate.

56. The semiconductor element according to claim 46, wherein the microcrystal located in the surface region is shaped in substantially a columnar shape.

57. The semiconductor element according to claim 46, wherein a film thickness of the silicon-based film is set to 1.0 nm or more and 20 nm or less.

5            54. The semiconductor element according to  
claim 46, wherein the silicon-based film containing  
the microcrystal includes a region in which the  
diffraction intensity of the (220) face of the  
microcrystal, which is measured with X rays or  
10 electron rays, occupies 80% or more of the total  
diffraction intensity.

55. The semiconductor element according to claim 46, wherein in the silicon-based film containing the microcrystal, a microcrystal which is preferentially oriented along the (220) face is shaped in a column extending in a vertical direction relative to the substrate.

20            56. The semiconductor element according to claim 46, wherein the microcrystal located in the interface region is shaped in substantially a sphere.

57. The semiconductor element according to  
25 claim 46, wherein a film thickness of the interface  
region is set to 1.0 nm or more and 20 nm or less.

58. The semiconductor element according to claim 46, wherein the silicon-based film containing the microcrystal contains at least one kind of oxygen atoms, carbon atoms and nitrogen atoms, and the total  
5 amount of the atoms is  $1.5 \times 10^{18}$  atoms/cm<sup>3</sup> or more and  $5.0 \times 10^{19}$  atoms/cm<sup>3</sup> or less.

59. The semiconductor element according to claim 46, wherein the silicon-based film containing  
10 the microcrystal contains  $1.0 \times 10^{19}$  atoms/cm<sup>3</sup> or more and  $2.5 \times 10^{20}$  atoms/cm<sup>3</sup> or less of fluorine atoms.

60. The semiconductor element according to claim 46, wherein the silicon-based film containing  
15 the microcrystal is formed by introducing a source gas containing at least one of a hydrogenated silicon gas and a fluorinated silicon gas, and hydrogen into a vacuum vessel, introducing high frequency into a high frequency introducing section in the vacuum  
20 vessel, and forming a silicon-based film on a substrate introduced into the vacuum vessel by a high frequency plasma CVD process.

61. The semiconductor element according to  
25 claim 60, wherein during the process of forming the silicon-based film containing the microcrystal, the flow rate ratio of the source gas is varied.



62. The semiconductor element according to  
claim 60, wherein the source gas is introduced into  
the vacuum vessel using a plurality of gas  
introducing sections, and the source gas flowing  
5 through at least one of the plurality of gas  
introducing sections has a flow rate ratio different  
from that in the other gas introducing sections.

63. The semiconductor element according to  
10 claim 60, wherein the high frequency is set to 10 MHz  
or more and 10 GHz or less.

64. The semiconductor element according to  
claim 63, wherein the high frequency is set to 20 MHz  
15 or more and 300 MHz or less.

65. The semiconductor element according to  
claim 60, wherein a distance between the high  
frequency introducing section and the substrate is  
20 set to 3 mm or more and 30 mm or less.

66. The semiconductor element according to  
claim 60, wherein a pressure under which the silicon-  
based film containing the microcrystal is set to  
25 formed is 100 Pa (0.75 Torr) or more and 5,000 Pa  
(37.5 Torr) or less.

67. The semiconductor element according to claim 60, wherein a residence time of the source gas during the formation of the silicon-based film containing the microcrystal is set to 0.01 second or more and 10 seconds or less.

68. The semiconductor element according to claim 67, wherein the residence time of the source gas during the formation of the silicon-based film containing the microcrystal is 0.1 second or more and 3 seconds or less.

69. The semiconductor element according to claim 60, wherein heating means used for the substrate in forming the silicon-based film containing the microcrystal is arranged opposite a surface of the substrate on which the silicon-based film containing the microcrystal is formed, and an output of the heating means decreases as the silicon-based film containing the microcrystal is formed.

70. A method of forming a silicon-based film containing a microcrystal, wherein a microcrystal located in at least one interface region of the silicon-based films containing the microcrystal has no orientation property.

71. The silicon-based film forming method according to claim 70, wherein in the silicon-based film containing the microcrystal, the ratio of the diffraction intensity of a (220) face of the microcrystal except for the non-orientation property region, which is measured with X rays or electron rays, to the total diffraction intensity changes in a film thickness direction of the silicon-based film.

72. The silicon-based film forming method according to claim 70, wherein the orientation property of the microcrystal located in the interface region is such that when measured with X rays or electron rays, three diffraction faces (111), (220), and (311) arranged in this order from the small angle side have such diffraction intensities that when the (111) face has a diffraction intensity of 1, the (220) face has a diffraction intensity of 0.50 or more and 0.60 or less, whereas the (311) face has a diffraction intensity of 0.25 or more and 0.35 or less.

73. The silicon-based film forming method according to claim 71, wherein the ratio of the diffraction intensity of the (220) face of the microcrystal in the silicon-based film containing the microcrystal, which is measured with X rays or

electron rays, to the total diffraction intensity is made relatively low in an initial stage of film formation.

5           74. The silicon-based film forming method according to claim 70, wherein the orientation property of the microcrystal changes continuously.

75. The silicon-based film forming method  
10 according to claim 70, wherein the silicon-based film containing the microcrystal includes a region in which the diffraction intensity of the (220) face of the microcrystal, which is measured with X rays or electron rays occupies 80% or more of the total  
15 diffraction intensity.

76. The silicon-based film forming method according to claim 70, wherein in the silicon-based film containing the microcrystal, a microcrystal  
20 which is preferentially oriented along the (220) face is shaped in a column extending in a vertical direction relative to the substrate.

77. The silicon-based film forming method  
25 according to claim 70, wherein the microcrystal located in the interface region is shaped in substantially a sphere.

78. The silicon-based film forming method according to claim 70, wherein a film thickness of the interface region is set to 1.0 nm or more and 20 nm or less.

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79. The silicon-based film forming method according to claim 70, wherein the silicon-based film containing the microcrystal contains at least one kind of oxygen atoms, carbon atoms and nitrogen atoms, and the total amount of the atoms is set to  $1.5 \times 10^{18}$  atoms/cm<sup>3</sup> or more and  $5.0 \times 10^{19}$  atoms/cm<sup>3</sup> or less.

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80. The silicon-based film forming method according to claim 70, wherein the silicon-based film containing the microcrystal contains  $1.0 \times 10^{19}$  atoms/cm<sup>3</sup> or more and  $2.5 \times 10^{20}$  atoms/cm<sup>3</sup> or less of fluorine atoms.

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81. The silicon-based film forming method according to claim 70, wherein the silicon-based film containing the microcrystal is formed by introducing source gas containing at least one of a hydrogenated silicon gas and a fluorinated silicon gas, and hydrogen into a vacuum vessel, introducing high frequency into a high frequency introducing section in the vacuum vessel, and forming a silicon-based film on a substrate introduced into the vacuum vessel

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by a high frequency plasma CVD process.

82. The silicon-based film forming method according to claim 81, wherein during the process of forming the silicon-based film containing the microcrystal, the flow rate ratio of the source gas is varied.

83. The silicon-based film forming method according to claim 81, wherein the source gas is introduced into the vacuum vessel using a plurality of gas introducing sections, and the source gas flowing through at least one of the plurality of gas introducing sections has a flow rate ratio different from that in the other gas introducing sections.

84. The silicon-based film forming method according to claim 81, wherein the high frequency is set to 10 MHz or more and 10 GHz or less.

85. The silicon-based film forming method according to claim 84, wherein the high frequency is set to 20 MHz or more and 300 MHz or less.

86. The silicon-based film forming method according to claim 81, wherein a distance between the high frequency introducing section and the substrate

is set to 3 mm or more and 30 mm or less.

5       87. The silicon-based film forming method  
according to claim 81, wherein a pressure under which  
the silicon-based film containing the microcrystal is  
formed is set to 100 Pa (0.75 Torr) or more and 5,000  
Pa (37.5 Torr) or less.

10       88. The silicon-based film forming method  
according to claim 81, wherein a residence time of  
the source gas during the formation of the silicon-  
based film containing the microcrystal is set to 0.01  
second or more and 10 seconds or less.

15       89. The silicon-based film forming method  
according to claim 88, wherein the residence time of  
the source gas during the formation of the silicon-  
based film containing the microcrystal is set to 0.1  
second or more and 3 seconds or less.

20       90. The silicon-based film forming method  
according to claim 81, wherein heating means for the  
substrate in forming the silicon-based film  
containing the microcrystal is arranged opposite a  
25       surface of the substrate on which the silicon-based  
film containing the microcrystal is formed, and an  
output of the heating means decreases as the silicon-

based film containing the microcrystal is formed.